

## Unprecedented chemical transformation: crystallographic evidence for 1,1,2,2-tetrahydroxyethane captured within an Fe<sub>6</sub>Dy<sub>3</sub> single molecule magnet

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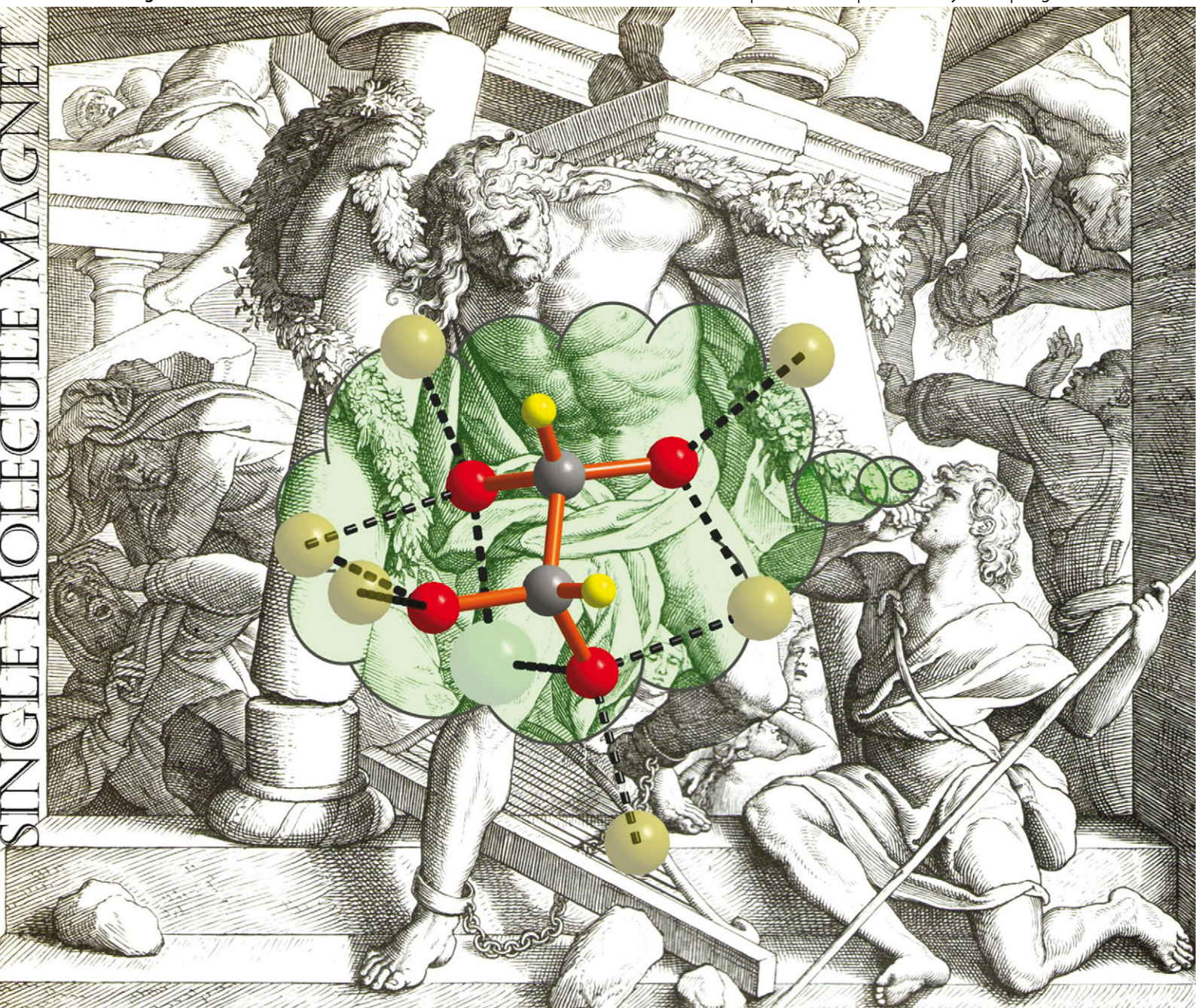


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**COMMUNICATION**

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Unprecedented chemical transformation: crystallographic evidence for 1,1,2,2-tetrahydroxyethane captured within an  $\text{Fe}_6\text{Dy}_3$  single molecule magnet



## COMMUNICATION

Unprecedented chemical transformation: crystallographic evidence for 1,1,2,2-tetrahydroxyethane captured within an Fe<sub>6</sub>Dy<sub>3</sub> single molecule magnet†

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**A nonanuclear {Fe<sub>6</sub>Dy<sub>3</sub>} coordination cluster displaying SMM behaviour in which an unprecedented chemical transformation provides structural information for the existence of 1,1,2,2-tetrahydroxyethane is reported.**

In the course of studying the electronic properties of various coordination compounds, the ongoing investigations of several research groups have resulted in the isolation of coordination compounds and clusters with interesting properties pointing towards potential technological applications. For example, sustained water oxidation photocatalysis can be achieved by a bioinspired molecular cluster,<sup>1</sup> lanthanide-based clusters are employed in optics as lasers and light-emitting diodes,<sup>2</sup> and polyoxometalates show *in vivo* antiviral activity<sup>3</sup> while many polynuclear compounds can be considered as molecule-based magnets.<sup>4</sup> In the field of molecular magnetism, the selection of the appropriate organic ligand to bridge metal centres for the synthesis of coordination clusters is a vital component, which has led to the investigation by a number of research groups into the coordination capabilities of organic molecules such as calixarenes,<sup>5</sup> phosphonates,<sup>6</sup> diols,<sup>7</sup> and triethanolamine-based ligands.<sup>8</sup>

In selecting flexible or semi-flexible organic molecules a rational design of a desirable product is not feasible because a slight change in the synthetic parameters (mole ratios, counterions and so on) may, and often does, result in different products. Nevertheless, this synthetic approach is recognised as the most effective way to discover unprecedented systems. Thus, interesting results, which could never be predicted or expected, can be obtained, indicating

that more systematic studies are required in order to understand the factors operating for a given reaction system. In this context and choosing triethanolamine as the organic ligand we have described the synthesis of a homometallic heptanuclear Fe<sub>7</sub> and its related octanuclear Fe<sub>8</sub> coordination cluster,<sup>9</sup> a heterometallic ferromagnetically coupled octanuclear [Fe<sub>4</sub>Dy<sub>4</sub>]<sup>10</sup> and hexanuclear Fe<sub>4</sub>Ln<sub>2</sub>,<sup>11</sup> where Ln = Er and Lu, ferromagnetically wheels. In addition, the icosanuclear [Fe<sub>16</sub>Ln<sub>4</sub>] where Ln = Sm, Eu, Gd, Tb, Dy, Ho<sup>12</sup> wheels as well as the undecanuclear Fe<sub>7</sub>Dy<sub>4</sub> coordination cluster show dominant antiferromagnetic coupling between the spin carriers as could be confirmed by variable-field <sup>57</sup>Fe Mössbauer spectroscopy.<sup>13</sup>

In this communication we report the synthesis, structure, magnetic properties and Mössbauer studies of a new heterometallic nonanuclear iron-dysprosium cluster displaying SMM behaviour and a *U*<sub>eff</sub> barrier of 65.1 K which is the highest so far observed for Fe–Ln systems. Furthermore, the unprecedented chemical transformation of part of the triethanolamine ligand to give a deprotonated 1,1,2,2-tetrahydroxyethane tetraanion has taken place and this is captured within the metallic core.

The reaction of [Fe<sup>III</sup><sub>3</sub>O(CH<sub>3</sub>COO)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>][NO<sub>3</sub>],<sup>14</sup> Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, triethanolamine (teaH<sub>3</sub>), and NaN<sub>3</sub> in a molar ratio of 1 : 3 : 3 : 12 : 18 in C<sub>2</sub>H<sub>5</sub>OH/(CH<sub>3</sub>)<sub>2</sub>CO (1 : 1) gave a red-orange solution from which orange crystals of the compound [Fe<sup>III</sup><sub>6</sub>Dy<sup>III</sup><sub>3</sub>(μ<sub>7</sub>-C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>)(μ<sub>4</sub>-tea)<sub>2</sub>(μ<sub>3</sub>-teaH)<sub>4</sub>(μ<sub>2</sub>-N<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>6</sub>(NO<sub>3</sub>)]·2EtOH, 1·2EtOH, were formed over several days<sup>15</sup> (where C<sub>2</sub>H<sub>2</sub>O<sub>4</sub><sup>4−</sup> is the tetraanion of 1,1,2,2-tetrahydroxyethane).

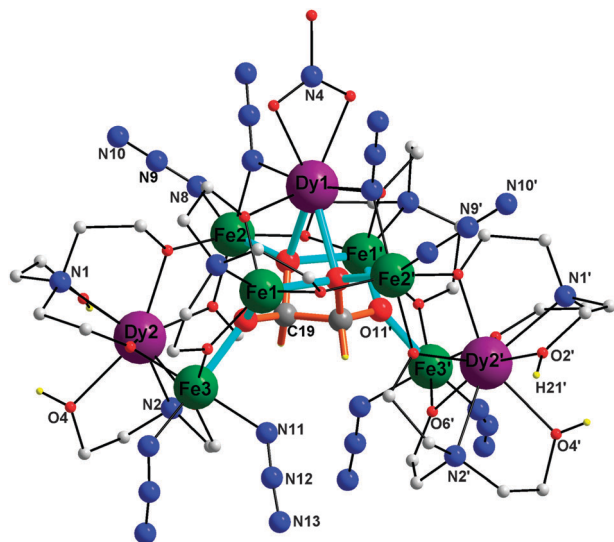
The structure of the coordination cluster 1 is shown in Fig. 1. Compound 1·2EtOH crystallizes in the orthorhombic space group *Pccn* with *Z* = 4.† The core of the cone-like nonanuclear cluster can be considered as an octanuclear distorted wheel built up from two dicationic [Fe<sup>III</sup><sub>3</sub>(tea)(N<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> trimers bridged by two monoanionic [Dy(teaH<sub>2</sub>)<sub>2</sub>]<sup>−</sup> units, while one dication [Dy(NO<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> caps the wheel. Notably, at the centre of the cone additional bridging is provided by the tetraanion of 1,1,2,2-tetrahydroxyethane. The Dy1 atom and the N4–O13 bond lie on a twofold axis which also passes through the midpoint of the C–C bond in the tetraanion of the 1,1,2,2-tetrahydroxyethane moiety. Each carbon atom (C19) of the tetraanion possesses an almost ideal tetrahedral geometry (see Table S1, ESI†), while the bond angles and distances are related to those

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† Electronic supplementary information (ESI) available: The structure of the 2,3,4M9-3 skeleton, coordination modes of ligands and Mössbauer spectra (Fig. S1–S3). CCDC 909149 (1). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc38006d



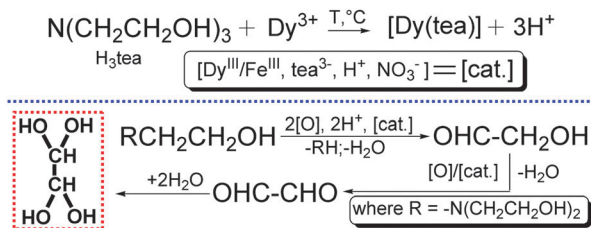
**Fig. 1** Molecular structure of **1** (two solvent  $\text{C}_2\text{H}_5\text{OH}$  molecules, some N atoms from disordered  $\text{N}_3$ -groups and H atoms from  $\text{CH}_2$ -groups were omitted for clarity). Symmetry code: (i)  $-x + 3/2, -y + 3/2, z$ .

reported previously.<sup>16</sup> Both Dy centres are 8-coordinate with dodecahedral and square antiprismatic geometry for Dy1 and Dy2, respectively. All Fe centres are 6 coordinate; Fe2 and Fe3 possess an almost ideal octahedral geometry while Fe1 possesses distorted octahedral geometry. The tetraanion acts as a scaffold for the core, bridging in total seven metal centres – the central Dy and all the Fe centres. Two  $\text{teaH}_2^-$  and one  $\text{tea}^{3-}$  ligands bridge three and four metal centres, respectively. There are two different coordination modes for the azide groups; two azides bridge Fe2 and Dy1 and their symmetry equivalents in an end-on-fashion while the other six azides are unidentate and fill the coordination environments of the Fe centres. Finally, one bidentate nitrate group completes the coordination sphere of Dy1 (Fig. S1, ESI†). Using our topological approach to describe coordination cluster cores we can enumerate this structure as **2,3,4M9-3** (Fig. S2, ESI†).<sup>17</sup>

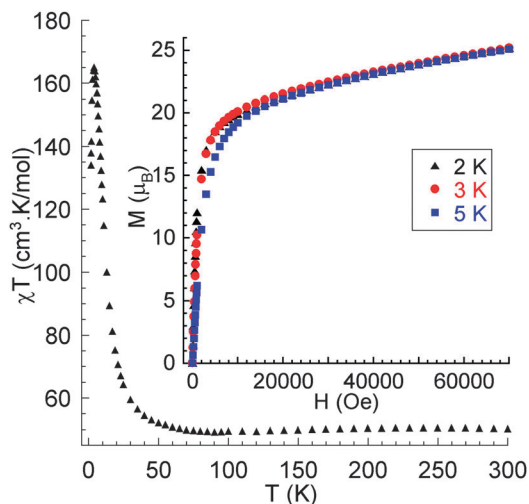
Analysing the synthetic protocol provides a possible explanation for the formation of the tetraanion of 1,1,2,2-tetrahydroxyethane. This could result from oxidation of solvent EtOH molecules. In order to check this, other experiments were performed in THF with trinuclear iron(III) trichloroacetate as starting material and a similar transformation was observed, suggesting a different origin for the tetraanion. Thus the alternative explanation for the formation of the anion is that the  $\text{teaH}_3$  ligand provides the  $-\text{CH}_2\text{CH}_2\text{OH}$  groups which lead to the captured tetraanion (see Scheme 1).

The static magnetic susceptibility of **1** was measured on a polycrystalline sample in the temperature range of 1.8–300 K in an applied field of 1 kOe (Fig. 2).

At room temperature, the  $\chi T$  product is  $50.51 \text{ cm}^3 \text{ K mol}^{-1}$ . This value is in good agreement with the expected value for the presence of the molecule of two units of three antiferromagnetically coupled iron(III) ions ( $S = 5/2, g = 2$ ) and three uncoupled  $\text{Dy}^{\text{III}}$  ions ( $S = 5/2, L = 5, {}^6\text{H}_{15/2}, g = 4/3$ ). Comparing these data with those obtained for an  $\text{Fe}_3\text{Ln}$  series,<sup>18a</sup> we conclude that the exchange coupling between iron ions within the chain has a comparable magnitude lying between  $-100$  and  $-50$  K. This is not unexpected taking into consideration very similar Fe–Fe distances and Fe–Fe–Fe angles in



**Scheme 1** A proposed mechanism of generation of ethane-1,1,2,2-tetraol under mild conditions in a  $\{\text{Fe}_6\text{Dy}_3\}$  (**1**) molecule.

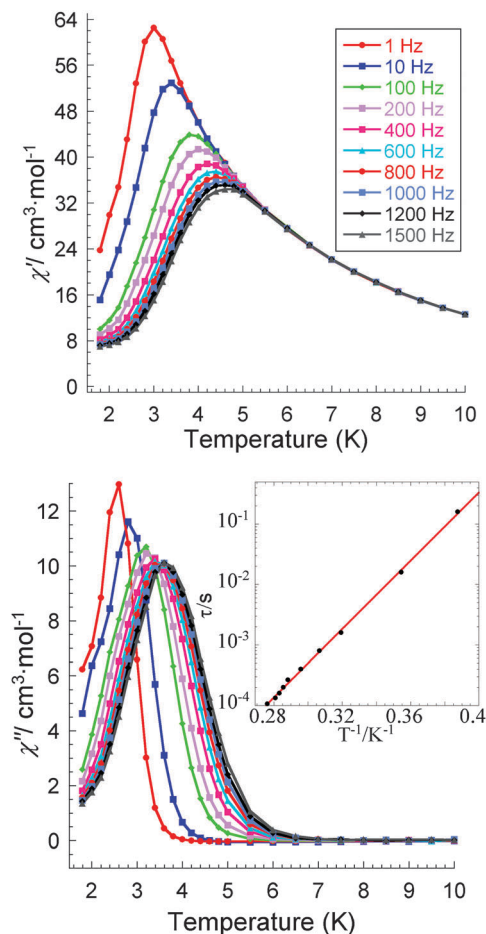


**Fig. 2** Plot of  $\chi T$  vs.  $T$  for complex **1** at 1 kOe. Inset:  $M$  vs.  $H$  data at 2, 3 and 5 K.

both systems. Upon cooling, the  $\chi T$  product slightly decreases to a minimum value of  $49.2 \text{ cm}^3 \text{ K mol}^{-1}$  at 90 K. Below 90 K, the  $\chi T$  product rises sharply to reach  $165.1 \text{ cm}^3 \text{ K mol}^{-1}$  at 4.0 K, indicative of ferromagnetic interactions, before it drops down to  $134.1 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.8 K. This behaviour is typically observed when ferromagnetic interactions between magnetic ions are dominant.

The field dependence of magnetization measurements at low temperatures reveals a relatively rapid increase in the magnetization at low fields ( $\sim 20.2 \mu_B$  around 10 kOe at 2 K) and then a linear increase without clear saturation (Fig. 2, inset), in good agreement with the expected value ( $3 \times 5.20 \mu_B$ ) for three isolated  $\text{Dy}^{\text{III}}$  ions and two antiferromagnetically coupled  $\text{Fe}_3$  chains ( $2 \times 5.0 \mu_B$ ). This value ( $\sim 25 \mu_B$ ) is lower than the expected saturation value of  $60 \mu_B$ , but close to that expected for such a combination of magnetic centers. The high field linear variation of  $M$  suggests the presence of a significant anisotropy or low lying excited states in this compound. Given the unexpected ferromagnetic behaviour, the dynamics of the magnetization were investigated from the ac susceptibility measurements in zero static field with a 3.0 Oe ac oscillating field. As shown in Fig. 3, an obvious temperature- and frequency-dependent ac signal is detected for **1**, indicating slow relaxation of magnetization expected for a single-molecule magnet.

The temperature dependence of the dynamic susceptibility was studied without an applied static field in the temperature range of 1.8–10 K. Fitting the data to an Arrhenius law, the



**Fig. 3** Temperature dependence of the in-phase signal,  $\chi'$  (top), out-of-phase signal,  $\chi''$  (bottom), and the resulting Arrhenius plot (inset) from the ac susceptibility measurements of **1** without an applied static field.

characteristic SMM energy gap,  $U_{\text{eff}}$ , has been estimated at 65.1 K and the pre-exponential factor,  $\tau_0$ , to be  $1.64 \times 10^{-12}$  s.

Our assumption about antiferromagnetic coupling within the two  $\text{Fe}_3$  chains was confirmed by Mössbauer spectroscopy at low temperature in external magnetic fields. The spectra at 3 K in zero and small applied external magnetic fields are easily fitted by three well-resolved subspectra with relative intensities of 1 : 1 : 1 (Fig. S3, ESI†). Such a profile is expected taking into account different ligand field environments around each Fe ion. For the two external sextets the total field at the nucleus  $H_{\text{eff}} = H_{\text{appl}} + H_{\text{hf}}$ , which is the sum of the applied ( $H_{\text{appl}}$ ) and magnetic hyperfine fields ( $H_{\text{hf}}$ ), decreases with increasing  $H_{\text{appl}}$ , and the sextets move inwards indicating a negative magnetic hyperfine interaction for these Fe ions. On the other hand, the magnetic hyperfine interaction for other Fe ions in the lower intensity subspectrum is positive and the sextet moves outwards. This opposite trend of the field dependence of the two Fe sextets as compared with the third one is a well known signature of antiparallel-spin-coupled iron molecular paramagnets.<sup>13,18,19</sup>

In summary, we have demonstrated the synthesis, structure, magnetic properties and Mössbauer studies of a new heterometallic nonanuclear iron dysprosium cluster. The formation of the unprecedented topological framework **2,3,4M9-3** was stabilized

by the capture within the metallic core of the tetraanion of a 1,1,2,2-tetrahydroxyethane molecule, generated from chemical transformation of triethanolamine. Least-squares fitting of data extracted from the ac out-of-phase signals to an Arrhenius equation gives the anisotropy energy barrier  $U_{\text{eff}} = 65.1$  K, which is the highest value reported so far for Fe–Ln SMMs.

Work is in progress to investigate properties of other congeners of this  $\{\text{Fe}_6\text{Ln}_3\}$  system as well as new Fe–Ln coordination clusters with unusual topologies and interesting magnetic properties.

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## Notes and references

† Crystal data for  $1 \cdot 2\text{C}_2\text{H}_5\text{OH}$ :  $\text{C}_{42}\text{H}_{90}\text{N}_{31}\text{O}_{27}\text{Dy}_3\text{Fe}_6$ ,  $M_r = 2284.05$ , orthorhombic, space group *Pccn* (no. 56),  $a = 13.9586(9)$  Å,  $b = 18.4257(14)$  Å,  $c = 28.917(3)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 7437.4(10)$  Å<sup>3</sup>,  $Z = 4$ .  $T = 298(2)$  K,  $D_c = 2.038$  g cm<sup>−3</sup>,  $F(000) = 4508$ ,  $R_1 = 0.0610$  (486 parameters),  $wR_2 = 0.1225$  [ $I \geq 2\sigma(I)$ ], GOF = 1.014 for all 7091 data.

- 1 R. Brimblecombe, G. F. Swiegers, G. C. Dismukes and L. Spiccia, *Angew. Chem., Int. Ed.*, 2008, **47**, 7335.
- 2 J.-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048.
- 3 J. T. Rhule, C. L. Hill, D. A. Judd and R. F. Schinazi, *Chem. Rev.*, 1998, **98**, 327.
- 4 J. S. Miller, D. Gatteschi (guest editors), Special themed issue “Molecule-based magnets”, *Chem. Soc. Rev.*, 2011, **40**, 3053.
- 5 S. Sanz, K. Ferreira, R. D. McIntosh, S. J. Dalgaro and E. K. Brechin, *Chem. Commun.*, 2011, **47**, 9042.
- 6 Y.-Z. Zheng, M. Evangelisti and R. E. P. Winpenny, *Chem. Sci.*, 2011, **2**, 99.
- 7 A. J. Tasiopoulos and S. P. Perlepes, *Dalton Trans.*, 2008, 5537.
- 8 S. K. Langley, L. Ungur, N. F. Chilton, B. Moubaraki, L. F. Chibotaru and K. S. Murray, *Chem.–Eur. J.*, 2011, **17**, 9209.
- 9 A. M. Ako, O. Waldmann, V. Mereacre, F. Klöwer, I. J. Hewitt, C. E. Anson, H. U. Güdel and A. K. Powell, *Inorg. Chem.*, 2007, **46**, 756.
- 10 D. Schray, G. Abbas, Y. Lan, V. Mereacre, A. Sundt, J. Dreiser, O. Waldmann, G. E. Kostakis, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2010, **49**, 5185.
- 11 S. Schmidt, D. Prodius, G. Novitchi, V. Mereacre, G. E. Kostakis and A. K. Powell, *Chem. Commun.*, 2012, **48**, 9825.
- 12 A. Baniodeh, I. J. Hewitt, V. Mereacre, Y. Lan, G. Novitchi, C. E. Anson and A. K. Powell, *Dalton Trans.*, 2011, **40**, 4080.
- 13 V. Mereacre, D. Prodius, Y. Lan, C. Turta, C. E. Anson and A. K. Powell, *Chem.–Eur. J.*, 2011, **17**, 123.
- 14 J. F. Duncan, C. R. Kanekar and K. F. Mok, *J. Chem. Soc. A*, 1969, 480.
- 15 Synthesis of  $[\text{Fe}^{\text{III}}_6\text{Dy}^{\text{III}}_3(\mu_7\text{-C}_2\text{H}_2\text{O}_4)_2(\mu_4\text{-tea})_2(\mu_3\text{-teaH})_4(\mu_2\text{-N}_3)_2(\text{N}_3)_6(\text{NO}_3)] \cdot 2\text{EtOH}$ :  $[\text{Fe}^{\text{III}}_6\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 3\text{H}_2\text{O}$  was prepared by the method described by Duncan *et al.*<sup>14</sup> Triethanolamine (425 mg, 2.85 mmol),  $[\text{Fe}^{\text{III}}_6\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 2\text{H}_2\text{O}$  (170 mg, 0.24 mmol),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (300 mg, 0.74 mmol), sodium azide (290 mg, 4.46 mmol) and  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (343 mg, 0.74 mmol) were dissolved under stirring in a mixture of 10 mL ethanol and 10 mL acetone. The cooled solution was filtered and left undisturbed in a sealed vial. After three days the red-orange single crystals suitable for X-ray analysis were collected and air dried. Yield: ~28 mg (~5% based on Dy). Anal. calc. for  $\text{C}_{40}\text{H}_{84}\text{N}_{31}\text{O}_{26}\text{Dy}_3\text{Fe}_6$  (loss of one solvent EtOH): C, 21.47; H, 3.78; N, 19.40; found: C, 21.43; H, 3.67; N, 19.46%. IR (KBr)/cm<sup>−1</sup>: 3401 (b, vs), 2970 (m), 2927 (m), 2865 (m), 2082 (vs), 2042 (vs), 1638 (b, w), 1513 (wm), 1470 (wm), 1384 (s), 1338 (m), 1289 (wm), 1263 (w), 1092 (s), 1072 (s), 1026 (m), 963 (m), 904 (ms), 832 (m), 746 (w), 632 (m), 605 (m), 584 (m), 493 (b, m).
- 16 V. W. Day, M. R. Thompson, C. S. Day, W. G. Klemperer and R.-S. Liu, *J. Am. Chem. Soc.*, 1980, **102**, 5971.
- 17 (a) G. E. Kostakis and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2686; (b) G. E. Kostakis, V. A. Blatov and D. M. Proserpio, *Dalton Trans.*, 2012, **41**, 4634.
- 18 (a) J. Bartolomé, G. Filoti, V. Kuncser, G. Schintea, V. Mereacre, C. E. Anson, A. K. Powell, D. Prodius and C. Turta, *Phys. Rev. B*, 2009, **80**, 014430G; (b) A. M. Ako, V. Mereacre, Y. Lan, C. E. Anson and A. K. Powell, *Chem.–Eur. J.*, 2011, **17**, 4366.
- 19 V. Mereacre, *Angew. Chem., Int. Ed.*, 2012, **51**, 9922.